

NOLC REPORT 738

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Effective 1 July 1967, the Naval Ordnance Laboratory, Corona, California became the Naval Weapons Center Corona Laboratories, Corona, California.

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CHEMOELECTRIC ENERGY CONVERSION FOR NONAQUEOUS RESERVE BATTERIES

Fifteenth Quarterly Report

JANUARY - MARCH 1967

RESEARCH DEPARTMENT

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NAVAL ORDNANCE LABORATORY CORONA
CORONA, CALIFORNIA

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NAVAL ORDNANCE LABORATORY CORONA

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FOREWORD

This report summarizes studies conducted during January through March, 1967, as part of continuing research on the conversion of chemical to electrical energy for application in Navy guided-missile auxiliary power supplies. The Electrochemistry Branch, Chemistry Division, Research Department, of the Naval Weapons Center Corona Laboratories (formerly the Naval Ordnance Laboratory Corona), is conducting this research under ORDTASK ORD-033-321/215-1/F009-06-04 and AIRTASK A34-340/211-1/R010-01-01. This work is reported to the Interagency Advanced Power Group, Power Information Center, on Project Briefs PIC 1011, PIC 1270, PIC 1545, and PIC 1614.

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ABSTRACT

The effects of H_2S and NH_4^+ on the reduction of sulfur in NH_3 solutions were investigated and both were found to be beneficial. The effects of various cathode materials and acid strengths on the reduction of m-DNB were also investigated and sulfamide and cyanamide were found to favorably affect the reduction of m-DNB, while urea did not.

Various electrode materials were tested in acid liquid ammonia to determine their value as catalysts for the electrochemical oxidation of carbonaceous fuels. Titanium and tantalum were found to offer wide potential ranges and good resistance to electrode corrosion. Methanol was tested in liquid $\text{NH}_3\text{-NH}_4\text{SCN}$ for possible oxidation on various electrode surfaces, but no activity was observed in liquid ammonia solutions.

CATHODE STUDIES FOR NONAQUEOUS FUEL CELLS

by

William S. Harris and Martha A. Hofmann

INTRODUCTION

During the past quarter (January through March, 1967), further studies have been conducted to investigate the use of sulfur and aromatic nitro compounds as cathodes in liquid ammonia fuel cells. Investigations were made to determine the following: the solubility and rate of solution of sulfur in both acid and neutral solutions, the effects of different acids and acid strengths on the reduction of sulfur and meta-dinitrobenzene (m-DNB), and the effects of different cathode materials on the reduction of m-DNB.

REDUCTION OF SULFUR

In previous experiments, research on the sulfur-ammonia system was performed using neutral solutions, because of their proven compatibility with active metal anodes as contrasted to the corrosive action of acid solutions. Recently, however, experiments have been performed using solutions of acid and H_2S . Table 1 presents a summary of the solubility rate, amount, and yield of S in various neutral and acid solutions. The rate of solution of S in ammonia is reported¹ to be dependent upon temperature and allotropic modifications.

Sulfur dissolves slowly in NaSCN , LiNO_3 , and NaI , and forms dichroic blue-red solutions which, when left standing, decompose to yellow solutions. In both neutral and acid solutions, the addition of H_2S causes rapid dissolution of S, which forms yellow to yellow-brown solutions similar in color to aqueous polysulfide solutions. Li_2S , when added to neutral solutions, has no apparent effect on the dissolution of S, and no soluble polysulfides are formed, as would be expected in aqueous solutions.

¹ A literature review was made by Eastman Kodak Co., Rochester, N. Y., under Contract NOrd 18249 QR-10, 14 December 1960. For cited originals see References 1, 2, and 3. A more recent original work is given in Reference 4.

TABLE 1. Solubility Characteristics of Sulfur

Solvent	Dissolution		Yield (e ⁻ /atom)
	Rate	Amount	
NH ₃	Slow	30%	*
NH ₄ SCN-NH ₃	None	None	*
Neutral Ammoniates	Slow	*	1
Ammoniates + H ₂ S	Rapid	20-30%	1 - 2
NaI-Li ₂ S	Slow	*	1/2 - 1

* Not measured.

Sulfur is insoluble in NH₄SCN solutions, and hence, is probably insoluble in other acid solutions (NH₄NO₃, NH₄Cl, etc.). although the addition of H₂S, even in miniscule amounts, causes S to be soluble in NH₄SCN solutions. Mole ratios of S/H₂S of 50 result in solution of the otherwise insoluble S which forms yellow solutions.

The importance of the use of acid in sulfur reduction is shown in Figure 1. Reduction was first attempted using very weak acid solutions, while a constant current was applied. The only acid used was H₂S, which was added with the sulfur. Very little reduction occurred as shown by the vertical curve on the left side of the graph. The cathode potential dropped to the potential of the evolution of Na for these solutions. When a stronger acid, NH₄I, was added, the sulfur was reduced as shown in the horizontal curve. As shown in Figure 1, both H₂S and NH₄⁺ play an important role in the reduction of sulfur. A factorial experiment is currently in progress to investigate the roles of these compounds.

REDUCTION OF NITRO COMPOUNDS

Two important aspects of the use of aromatic nitro compounds, specifically, m-DNB, were investigated and are reported here.

Effect of Cathode Material

Four different metals were employed as cathodes for the reduction of m-DNB in a neutral ammonia solution, NaSCN, at constant current. The observed results with these metals (Pt, Hg, Cu, and Ni) were the

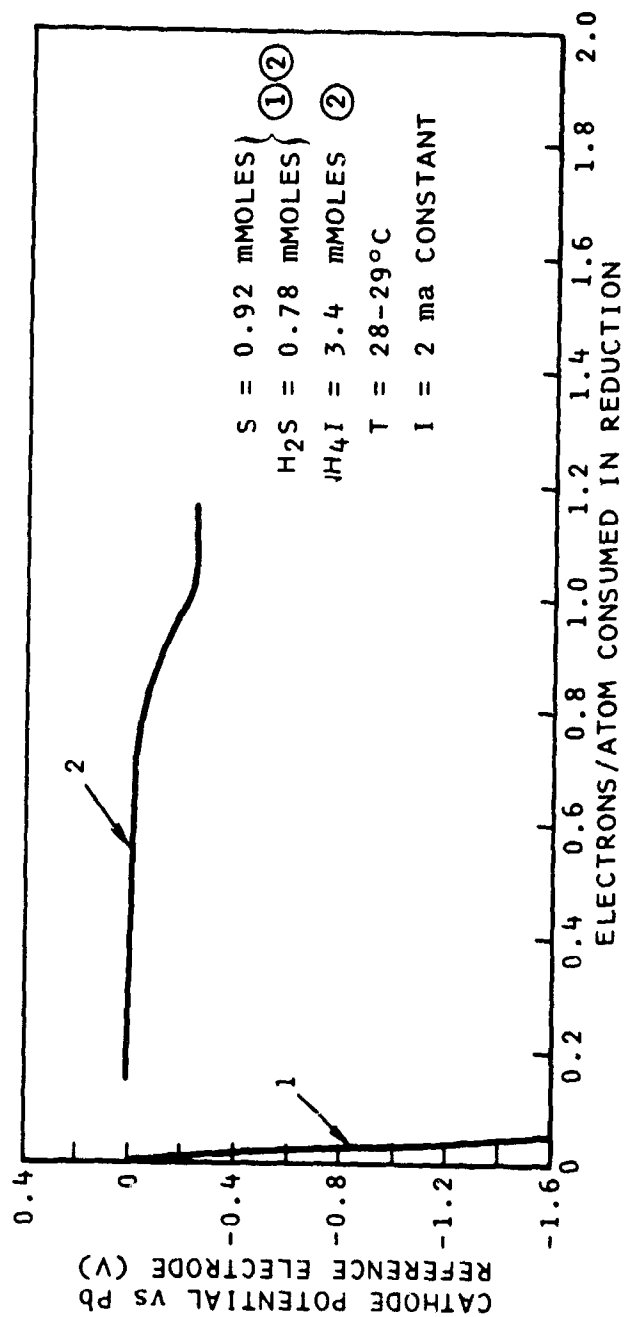
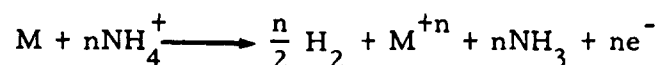


FIGURE 1. Sulfur Reduction in NaI Ammoniate

same within the expected experimental variations and agree with previous reductions on Hg which yielded less than $2e^-$ /molecule of m-DNB.

Effect of Acid Strength

It is generally known that acid is necessary for the efficient utilization of aromatic nitro compounds in the liquid ammonia systems. Excess acid in the vicinity of the metal or metal-ammoniate anode, is to be avoided, however, because of the deleterious parasitic reaction of metal dissolution, which is expressed by



where M is the electrode metal. For this reason, acids of different strength were investigated to determine the cathode reaction in their presence. Figure 2 shows the effects of different acids on the reduction of m-DNB. Three different acids were added to solutions of NaSCN (a neutral solution) in an excess amount compared to the stoichiometric amount needed for reaction during the reduction of the m-DNB. Urea, a slightly basic compound in aqueous solution, is expected to be a weak acid in liquid ammonia and is observed to have but little effect on the reduction. Sulfamide and cyanamide (slightly acid in aqueous solutions) are expected to be acidic in ammonia but not as strongly acidic as NH_4^+ , and are observed to favorably affect the reduction. These compounds are relatively lightweight dibasic acids in the ammonia system.

Since sulfamide and cyanamide are weaker acids than the ammonium salts typically employed in batteries, they should cause less corrosion when used with an active metal or metal-ammoniate anode.

WORK IN PROGRESS

As mentioned previously, the effects of acid and H_2S on S reduction are being investigated by means of a two-level, two-variable, statistically designed experiment.

Other workers have given evidence of reaction (such as color changes and generation of free radicals) between m-DNB and thiocyanate solutions. Experiments are in progress in which the coulometric yield of m-DNB is being studied as a function of the length of time it has been in NaSCN or NH_4SCN solution. A significant decrease in yield has been observed.

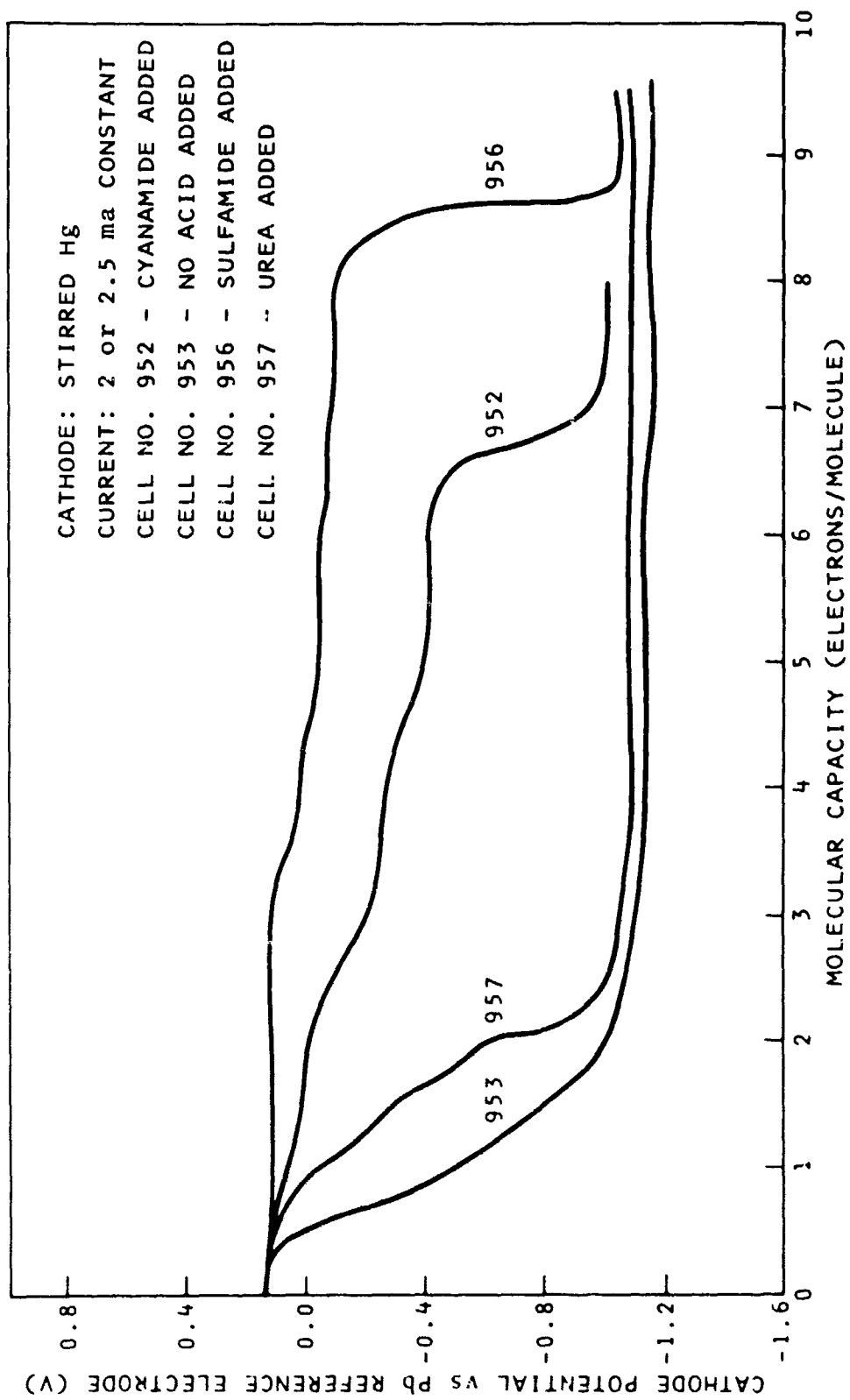


FIGURE 2. Reduction of m-DNB in NaSCN Ammoniate With Various Acids Added

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FUEL CELL REVIEW AND RESEARCH

by

M. H. Miles

INTRODUCTION

During the past quarter, development of fuel cells as independent electrical power sources for military aircraft and underwater vehicles has continued, with emphasis being placed on the investigation of carbonaceous fuels in nonaqueous electrolytes. Tests were made of various electrode materials in acid liquid ammonia solutions to determine those materials with useful potential ranges and high corrosion resistance. Tests were also made to determine the possible oxidation of carbonaceous fuels on the various electrode materials investigated.

Prior to conducting the reported tests, a literature review was made of current investigative trends. A summary of the existing data, and a discussion of the relative advantages and disadvantages of various types of fuel cell components is given in the following section.

CARBONACEOUS FUEL CELL LITERATURE REVIEW

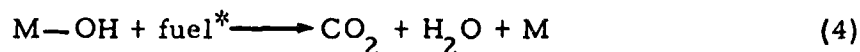
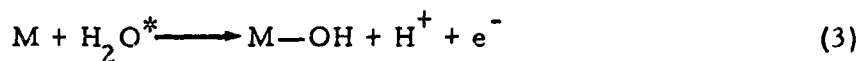
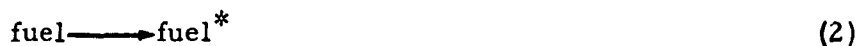
The four fundamental components of any fuel cell are the reactants, the catalysts, the electrodes, and the electrolyte. The assembly of a fuel cell requires the selection of these four components from a wide range of possibilities. Initially, the reactants are restricted to carbonaceous fuels and oxygenic oxidants; metal/air and metal/halogen systems are excluded.

The high temperature fuel cell using a molten electrolyte gave the first practical evidence that a carbonaceous fuel could be active; operating temperatures are 500-600°C for a molten carbonate electrolyte, as contrasted with above 1000°C for solid-oxide systems. The main advantage of high temperature systems is the fast electrode processes which reduce the catalytic requirements. A serious problem is caused by thermal cracking of the hydrocarbon fuels which forms carbon deposits on the electrode and in the fuel lines. The usual solution is to convert the hydrocarbon to H_2 and CO in a prereactor, by the process of steam reforming, and then feed the H_2 and CO to the fuel cell; this, however, reduces the active fuel cell efficiency. Certain fuels, such as kerosene, can be utilized without steam reforming as very little carbon is deposited.

During the past few years the trend has been toward the use of carbonaceous fuels with aqueous electrolytes. The lower operating temperatures ($T < 200^{\circ}\text{C}$) result in slower electrode processes, hence the selection of a catalyst becomes important. To reduce concentration polarization, strong acid (H_2SO_4) or base (KOH) electrolytes are used, but both have disadvantages. The CO_2 produced in oxidation of the fuel reacts with the basic electrolyte to produce carbonates, necessitating eventual replacement or regeneration of the electrolyte. An aqueous-acid electrolyte has the advantage of CO_2 rejection, but corrosion of the fuel cell components and of the catalyst are problems. To avoid these difficulties, aqueous carbonate electrolytes have been investigated, of which cesium and rubidium carbonates have proved satisfactory for use with fuels such as ethylene and methanol. Equilibrium mixtures of bicarbonate-carbonate are formed which reject CO_2 , and the high boiling points of Cs_2CO_3 and Rb_2CO_3 solutions permit operating temperatures of up to 200°C .

The use of a fuel that is soluble in the electrolyte has definite advantages. A soluble fuel simplifies the electrode construction and fuel introduction, and permits greater ease of transport and of fuel storage. Most investigations of soluble fuels have centered on methanol, ammonia, and hydrazine (Reference 1). The physical properties of methanol approach the ideal for a liquid fuel, and an expanded market for methanol is anticipated as a result of fuel cell use. Oxygen or air is generally employed as the oxidant in methanol fuel cells, but soluble oxidants such as NaClO_2 , KClO_2 , and H_2O_2 have also been successfully tested.

The reaction mechanisms for the electrochemical oxidation of carbonaceous fuels are not well understood. Many investigators believe the electron transfer is between the electrode and solvent rather than directly between the electrode and the fuel molecule. A generalized scheme (Reference 2) is



where the asterisk (*) indicates that the species is adsorbed on the electrode, "fuel" refers to any of the carbonaceous compounds, and M represents the electrode.

The electrode is an important variable in the oxidation of a fuel as it must adsorb the reacting species. The relationships between electrode catalytic activity and factors such as heat of adsorption and d-bond vacancies have attracted attention (Reference 3), but the selection of a catalyst for the electrochemical oxidation of a carbonaceous fuel remains largely a matter of experiment. The importance of the electrode is illustrated in the oxidation of methanol in aqueous KOH. Electrochemical oxidation takes place readily on platinum and palladium, but the process does not occur on many other surfaces such as gold, nickel, and tungsten.

THEORETICAL APPROACH AND WORK PLAN

The use of carbonaceous fuels with nonaqueous electrolytes is an unexplored area of fuel cell research. A different reaction mechanism for soluble fuels is a distinct possibility. Catalysts other than platinum could be effective in nonaqueous electrolytes. Furthermore, the solubilities of the fuels will be different so that fuels insoluble in water may be tested as soluble fuels. A logical first choice for the electrolyte would be liquid ammonia since the specific conductance of salts dissolved in this solvent is comparable with the specific conductance of aqueous solutions.

Thermodynamically, liquid ammonia has only a 0.04 V potential difference at 25°C between the electrochemical reactions which yield H_2 and N_2 (Reference 4). Fortunately, the kinetics of these decomposition reactions are very slow on most metal surfaces so that a much larger potential range is available for electrochemical studies before the decomposition reactions cause serious interference. This "overvoltage" is different for various electrode materials (Reference 5). The different overvoltages of various metals are attributed to differences in ΔH^\ddagger , the heat of activation of the rate-determining process. The higher the value of ΔH^\ddagger , the greater the overvoltage (Reference 6).

The oxidation of the electrode may also constitute a barrier in carbonaceous fuel cell research, since potential regions where large scale corrosion of the electrode occurs are useless for electrochemical studies.

Various metals will be investigated in acid and neutral liquid ammonia to determine their utility in fuel cell research and their useful potential ranges. Most of the metals of the short transition series will be investigated, and it is hoped that the electrochemical characteristics of each of these can be related to their position in the periodic table. The study will also include other electrode materials such as pyrolytic graphite, nickel boride, sodium tungsten bronzes, and metal alloys.

The carbonaceous fuels to be investigated in liquid ammonia are soluble hydrocarbons, hydroxy compounds, ethers, ketones, carboxylic acids, and amines. These fuels will be investigated on the various electrode surfaces found useful in liquid ammonia.

Hydrogen bonding substances such as sugars, esters, amines, and phenols are very soluble in liquid ammonia because of the tendency of ammonia to form hydrogen bonds. The basic character of ammonia is largely responsible for the high solubility of carboxylic acids and alcohols in liquid ammonia. London dispersion forces make ammonia a better solvent than water for non-polar molecules, particularly those with many electrons (Reference 7). Acetylene, for example, is very soluble in liquid ammonia but only slightly soluble in water. These properties of liquid ammonia can be used as a guide in selecting soluble fuels.

Exotic, inorganic fuels should also be investigated. Sodium tetrahydroborate (NaBH_4) will be one of the initial choices. It is very soluble in liquid ammonia and forms solutions of low vapor pressure. Perhaps it could be used as both the electrolyte and the fuel. Other strong reducing agents such as lithium aluminum hydride (LiAlH_4) should also be tested as possible fuels. Hydrazine is another possible soluble fuel for a fuel cell using liquid ammonia as the electrolyte. Liquid ammonia itself could be used as the fuel if an effective catalyst could be found for the oxidation of the solvent to N_2 .

EXPERIMENTAL TESTS AND RESULTS

Electrode Study

The following electrode materials were investigated in acid liquid ammonia solutions ($\text{NH}_3\text{-NH}_4\text{SCN}$): titanium, tantalum, tungsten, platinum, molybdenum, gold, nickel, silver, cobalt, copper, zinc, type 302 stainless steel, pyrolytic graphite, and a platinum-iridium alloy (95% Pt, 5% Ir).

The electrolyte solution was prepared by passing ammonia gas into the dried NH_4SCN salt to form a Diver's solution of low vapor pressure (Reference 8).

A lead-wire reference electrode and a platinum counter electrode were used in a three-compartment cell similar to one described previously (Reference 9).

Cyclic voltammetry was used to characterize the various electrode materials in the $\text{NH}_3\text{-NH}_4\text{SCN}$ solutions. The potential sweep rate was 125 mV/sec. The temperature was ambient (25-30°C). Figures 1-4

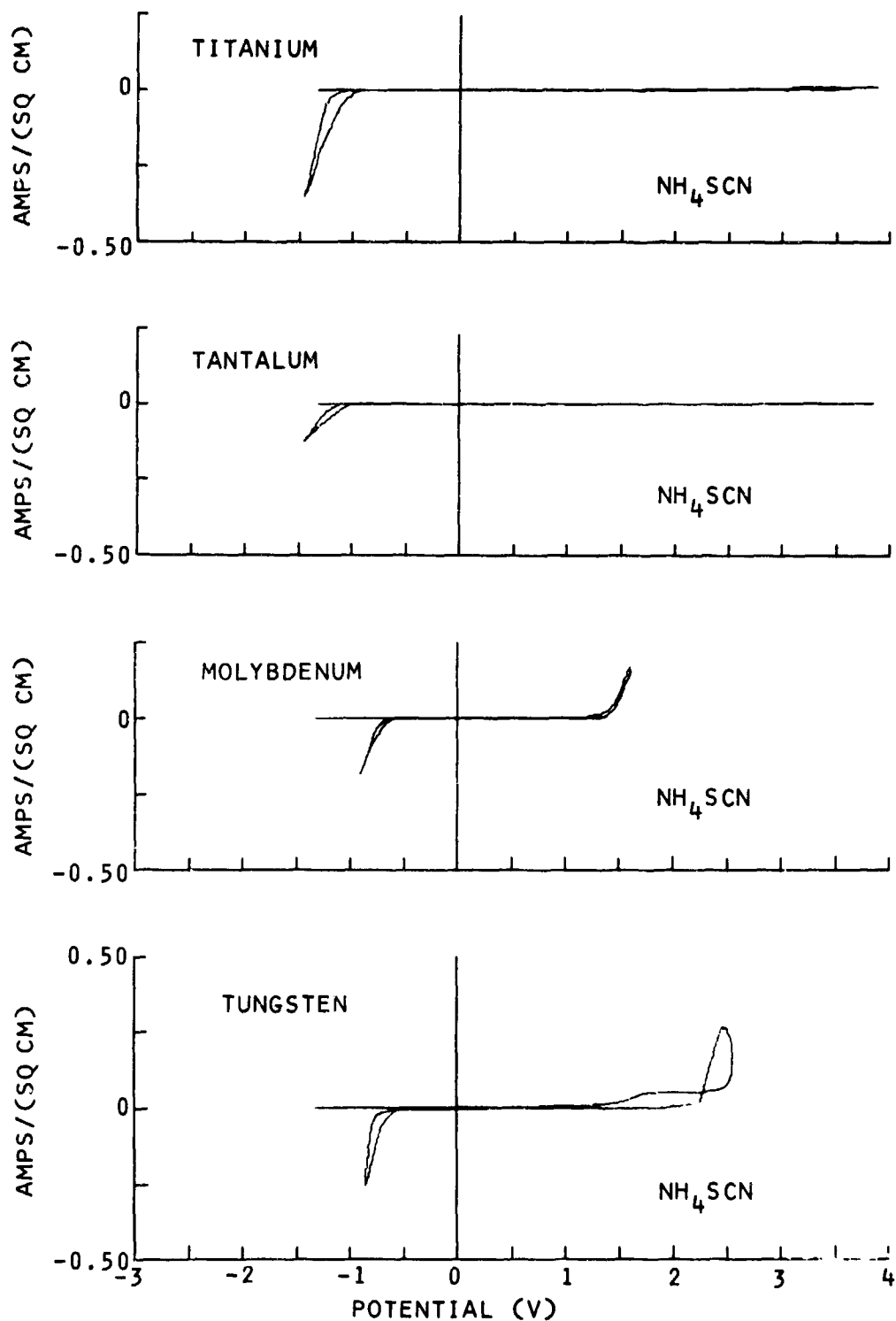


FIGURE 1. Current Density-Potential Traces in $\text{NH}_3\text{-NH}_4\text{SCN}$ for Ti, Ta, Mo, and W Electrodes

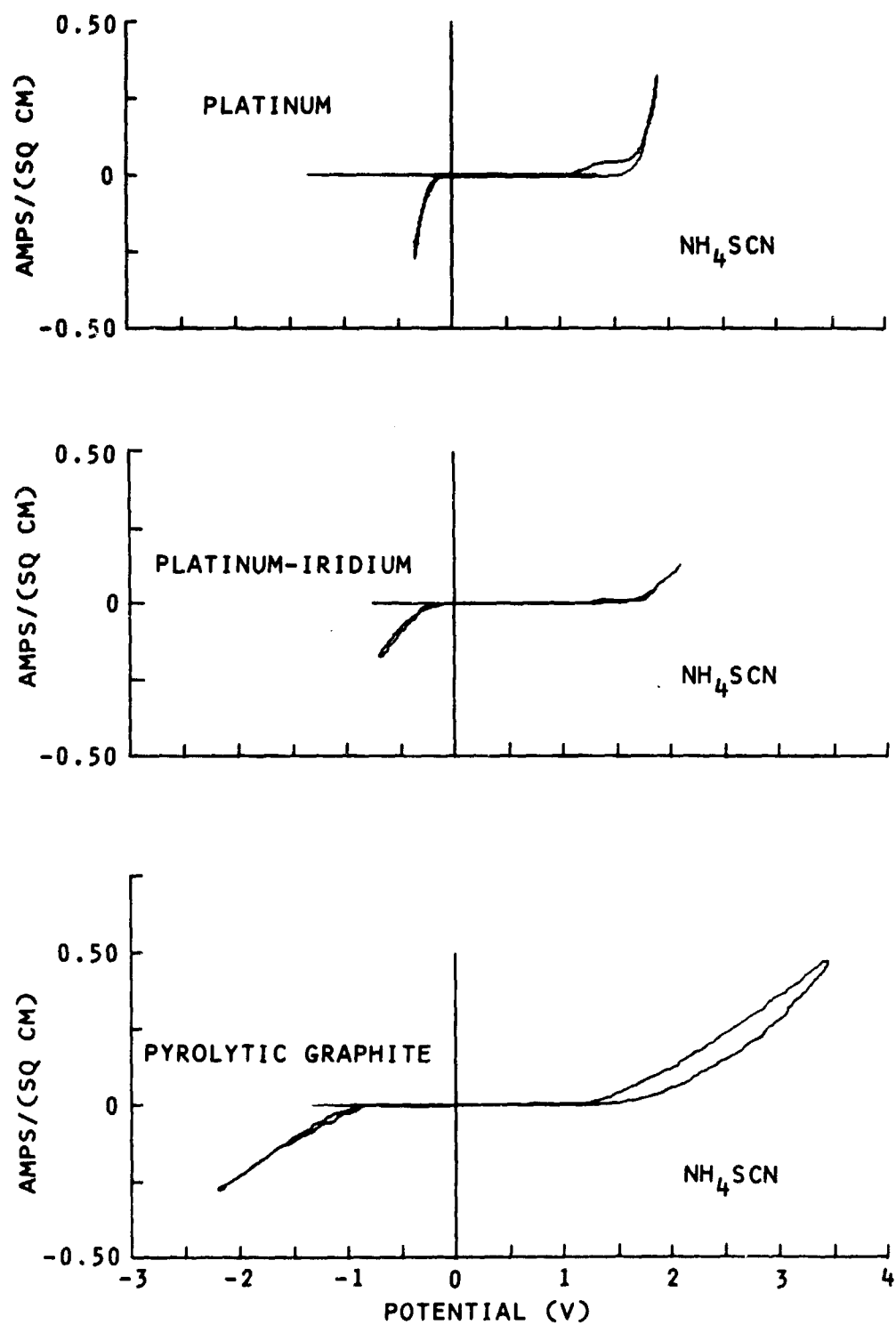


FIGURE 2. Current Density-Potential Traces in NH_3 - NH_4SCN for Pt, Pt-Ir, and Pyrolytic Graphite Electrodes

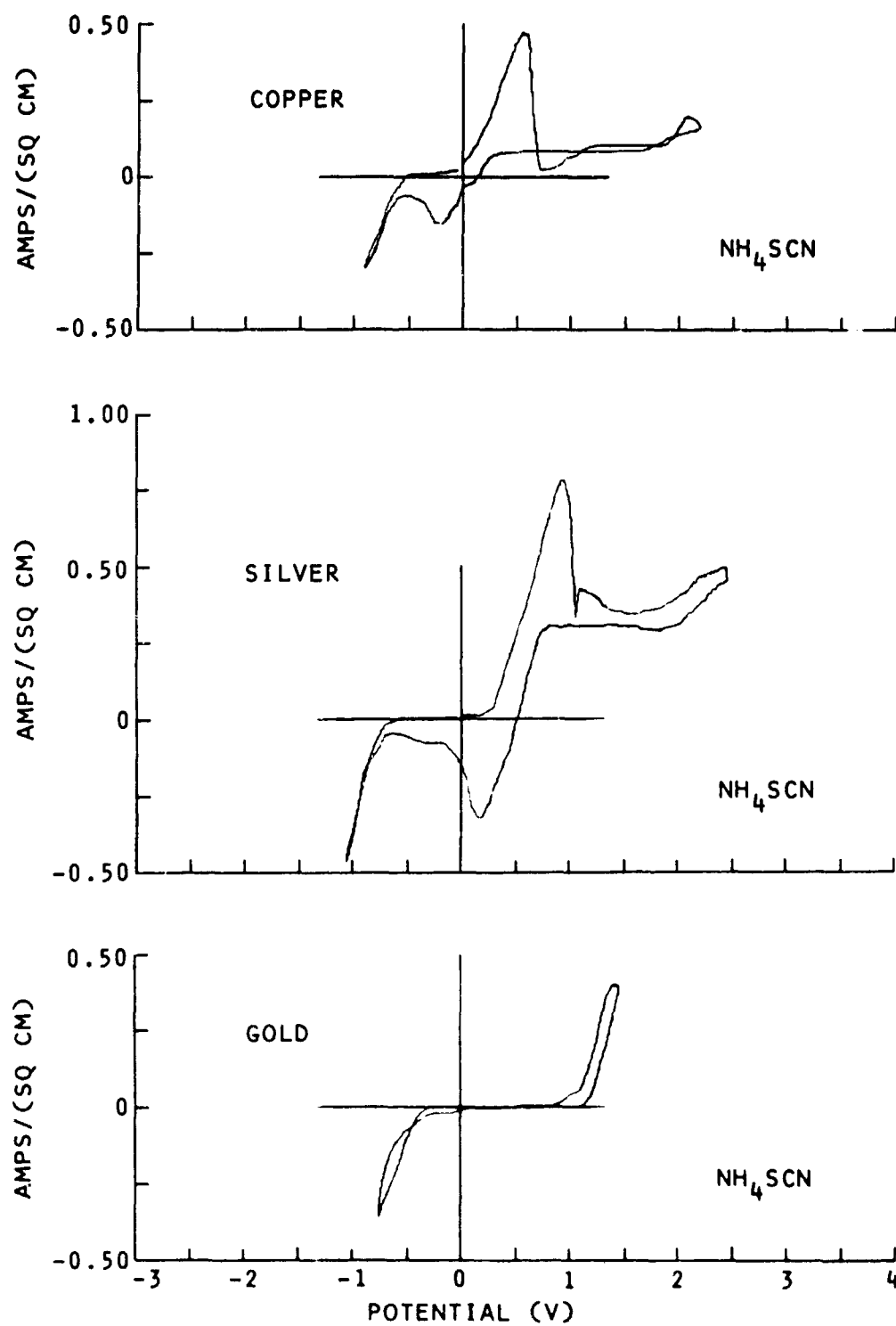


FIGURE 3. Current Density-Potential Traces in $\text{NH}_3\text{-NH}_4\text{SCN}$ for Cu, Ag, and Au Electrodes

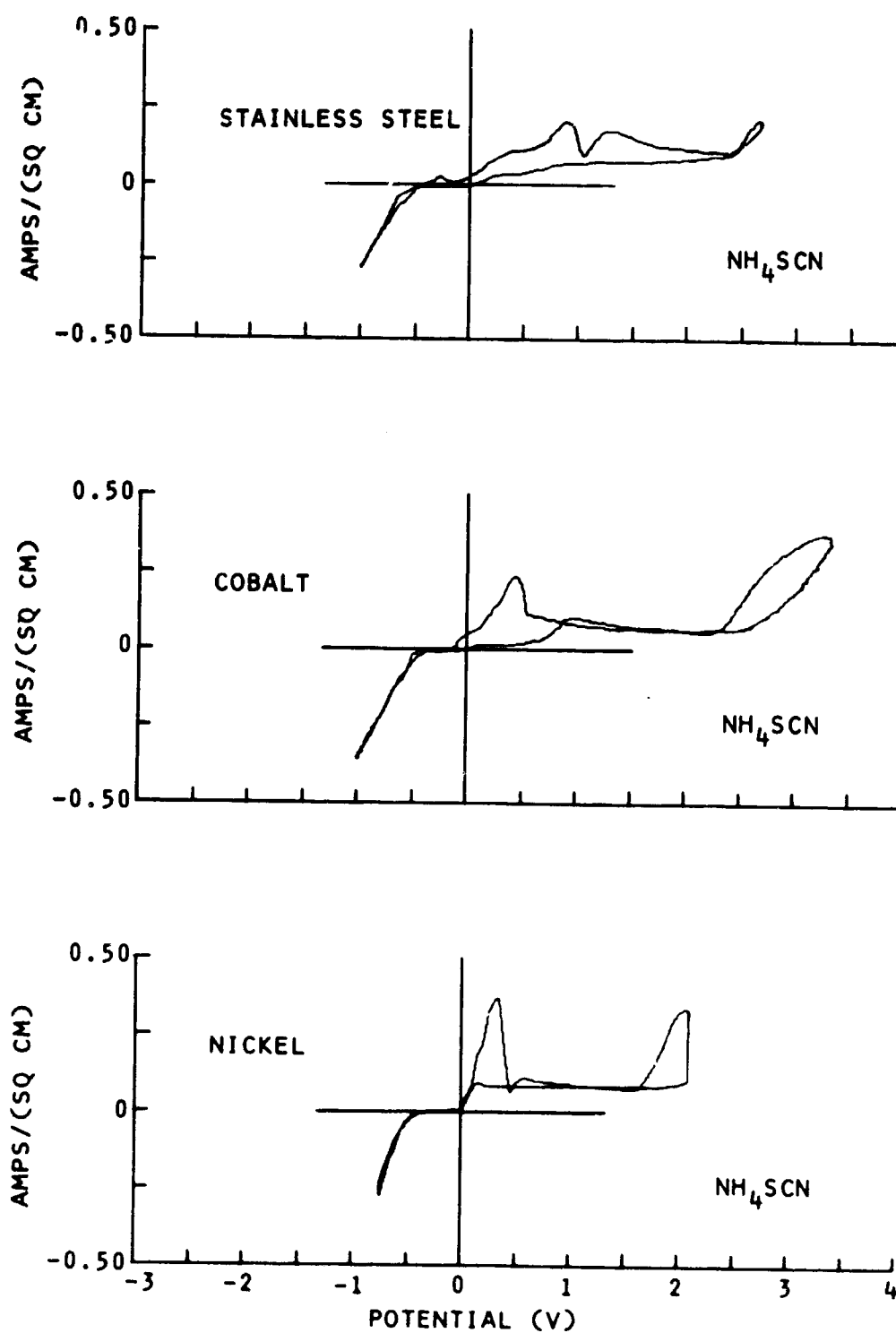


FIGURE 4. Current Density-Potential Traces in $\text{NH}_3\text{-NH}_4\text{SCN}$ for Stainless Steel, Co, and Ni Electrodes

present the results of these experiments. The current density is based upon the geometric area of the electrodes and the scale (y-axis) has been purposely made relatively insensitive so that only solvent decomposition and large scale electrode corrosion is revealed. The flat regions of Figures 1-4 indicate the useful potential ranges of the various electrodes in the $\text{NH}_3\text{-NH}_4\text{SCN}$ solution. The decomposition potentials are given in Table 1. These values are defined as the individual anodic or cathodic potentials required to achieve an arbitrary value of current density, as suggested by Foley (Reference 10). The value of current density selected was 0.1 amp/cm^2 .

TABLE 1. Decomposition Potentials for Various Electrodes in Liquid $\text{NH}_3\text{-NH}_4\text{SCN}$

Electrode	Decomposition Potential (volts) ^a		Range (volts)
	Anodic	Cathodic	
Tantalum	> 4.0	-1.4	> 5.4
Titanium	> 4.0	-1.3	> 5.3
Tungsten	2.6	-0.8	3.4
Pyrolytic Graphite	1.8	-1.4	3.2
Platinum-Iridium	2.0	-0.5	2.5
Molybdenum	1.5	-0.8	2.3
Platinum	1.8	-0.3	2.1
Gold	1.2	-0.6	1.8
Silver	0.4 ^b	-0.8	1.2
Type 302 Stainless Steel	0.3 ^b	-0.7	1.0
Cobalt	0.2 ^b	-0.6	0.8
Copper	0.1 ^b	-0.7	0.8
Nickel	0.1 ^b	-0.6	0.7

^a Measured against a Pb wire reference electrode. The potential required to achieve a current density of 0.1 amp/cm^2 at a sweep rate of 125 mV/sec . $T \sim 27^\circ\text{C}$.

^b Limited by electrode corrosion rather than solvent decomposition.

Titanium, tantalum, molybdenum, tungsten, platinum, platinum-iridium, pyrolytic graphite, and gold are all useful electrode materials for fundamental electrochemical studies in liquid $\text{NH}_3\text{-NH}_4\text{SCN}$ solutions. Titanium and tantalum both offer wide potential ranges and very high overvoltages for nitrogen evolution, as shown in Figure 1. The metals shown (Figure 1) are all located on the left-hand side of the periodic table and offer good resistance to electrode corrosion in liquid $\text{NH}_3\text{-NH}_4\text{SCN}$ solutions.

Platinum (Figure 2), as expected, has the lowest overvoltage for hydrogen evolution. An electrode oxidation peak is observed on platinum and platinum-iridium in $\text{NH}_3\text{-NH}_4\text{SCN}$ at about +1.45 V against the Pb wire reference electrode. As contrasted with platinum, pyrolytic graphite gave only slight gas evolution during the anodic sweep despite the high current density obtained.

The anodic and cathodic current densities on pyrolytic graphite increase more gradually than on the metal electrodes. This limits the usefulness of the pyrolytic graphite electrode for fundamental electrochemical investigations, since sensitive current density scales that are possible with metal electrodes cannot be used.

Figure 3 shows the current density-potential traces for the Group 1B metals. Corrosion greatly limits the usefulness of copper and silver as electrodes for fundamental electrochemical studies in $\text{NH}_3\text{-NH}_4\text{SCN}$ solutions. Sweeping with the copper electrode causes the $\text{NH}_3\text{-NH}_4\text{SCN}$ solution to gradually turn blue. The silver electrode gave the largest anodic peak current density and dissolved quite readily with repeated potential sweeps.

Stainless steel, cobalt, and nickel (Figure 4) are all limited by their low corrosion-resistance in $\text{NH}_3\text{-NH}_4\text{SCN}$ solutions. Repeated potential sweeps with the stainless steel or cobalt electrode cause the $\text{NH}_3\text{-NH}_4\text{SCN}$ solution to gradually turn orange in color.

The current density-potential traces shown in Figures 1-4 were obtained using a general purpose plotting program and CALMA Digitizer with an IBM System 360/50 Computer. This provided a convenient means of converting the original traces to a common current density scale (based upon geometrical electrode areas).

Fuel Study

The initial choice of a fuel to investigate in liquid $\text{NH}_3\text{-NH}_4\text{SCN}$ was methanol. Cyclic voltammetry was used to check possible oxidation of this fuel on the various electrode surfaces reported above. No activity was observed. It is suspected that ammonia poisons the platinum surface

and prevents the adsorption of methanol thereon. Definite activity for the oxidation of methanol on platinum in aqueous KOH solutions was observed, but this activity disappeared when the electrode was soaked in ammonia, indicating a poisoning effect by the ammonia.

Formic acid was screened on platinum, tungsten, and pyrolytic graphite. No oxidation was observed.

CONCLUSIONS AND RECOMMENDATIONS

Most fuel cell research to date has centered on systems with molten salt, solid oxide, or aqueous electrolytes. None of these are satisfactory at low temperatures. Molten salt and solid oxide systems require temperatures above 500°C, and aqueous systems suffer from rapid decrease in conductivity as the temperature drops below 0°C (some aqueous batteries lose 15-20% of their rated capacity at -2°C).

Research on nonaqueous electrolyte systems demands attention, and may lead to fuel cells operating at the low temperatures encountered in military operations and underwater activities. Possible nonaqueous solvents include liquid ammonia, acetone, sulfur dioxide, and pyridine. There is an enormous amount of research to be done in this area to determine what reactants and catalysts are active in these nonaqueous electrolytes, and also to determine the reaction mechanisms of the active materials.

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13. ABSTRACT <p>→ The effects of H_2S and NH_4^+ on the reduction of sulfur in NH_3 solutions were investigated and both were found to be beneficial. The effects of various cathode materials and acid strengths on the reduction of m-DNB were also investigated and sulfamide and cyanamide were found to favorably affect the reduction of m-DNB, while urea did not.</p> <p>Various electrode materials were tested in acid liquid ammonia to determine their value as catalysts for the electrochemical oxidation of carbonaceous fuels. Titanium and tantalum were found to offer wide potential ranges and good resistance to electrode corrosion. Methanol was tested in liquid NH_3-NH_4SCN for possible oxidation on various electrode surfaces, but no activity was observed in liquid ammonia solutions.</p>			

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